

CERAMIC MATERIALS BASED ON SYNTHETIC CALCIUM PHOSPHATE FOR MEDICAL USES

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Annotation. This article discusses the different methods of synthesis of hydroxyapatite and receiving on its base of ceramic materials in various ways. We have also developed our own technology. The conditions of compatibility and saddle the assumption and the suitability of the material for implantation.

Currently, there are a large number of implants used to replace bone defects, as well as its full replenishment. Existing metal implants (Ti, Ti-Ni) are widely used in medicine, but result in significant postoperative complications. Hence, the medical issue is to improve the technology of resorbable implants. However, the lack of suitable materials limits the improvement and development of certain types of implantable endoprosthesis.

The aim of this work is to develop the technology of synthetic hydroxyapatite for its use bioceramic materials and components for filling bone defects.

Biocompatibility, unique activity, structural and mechanical similarity of human bone tissue allows synthetic hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP) to be widely used in modern medicine, and materials science [1]. This property is characteristic not only of hydroxyapatite, but of all the calcium phosphate phosphoric acid. However, compared to DCPA and DCPH, which have low strength in composites it is more preferred to use crystalline hydroxyapatite.

There are many ways to obtain HAP as amorphous and as crystalline [4]. However, most preferably the preparation of amorphous hydroxyapatite as crystalline HAP is resorbed over a sufficiently long time, has poor osteoconductive, and methods of its production is quite labor-intensive.

It is obvious that for the synthesis of HAP, it is necessary to maintain the stoichiometric ratio $n(\text{Ca}^{2+})/n(\text{PO}_4^{2-}) = 1,67$, and pH not less than 8,37, to neutralize the nitric acid formed as isoelectric located at about a given value of pH.

Comparative X-ray diffraction are shown in Figure 1.

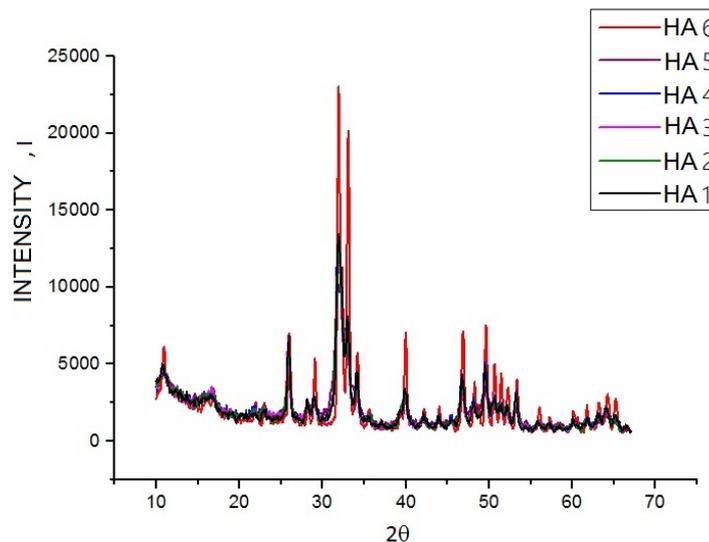
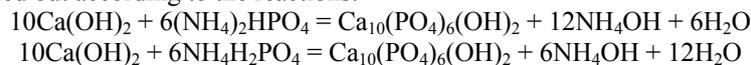


Fig. 1. A comparative chart of X-ray 6 samples

HA-1 hydroxyapatite synthesized by the classical drip synthesis technology of hydroxyapatite [2]. Methods of synthesis described in detail in the source. HA-2 and HA-3 were obtained by the first method of synthesis, however, the complete draining of mixtures were produced and pH was adjusted for 10 minutes before the stabilization, pH = 8,73. Solution was brought to a temperature of 60 ° C, and then part of the mixture remained aging for one day the mother liquor (HA-3), the other part was filtered off and washed once and the precipitate was dried (HA-2). HA-4 was obtained by heating treatment instead of heating on the heating surface in a flask similar to the synthesis of HA-1, the microwave heating at 200 watts of power and time of 30 minutes. These conditions are chosen experimentally and correspond to the time of the boiling beginning of the 1 liter mixture with the sample of 50 grams, after the precipitate was subjected to decantation, filtered, washed and dried. HA-5 is derived from calcium saccharate by a similar synthesis. [3] HA-6 obtained by a modified procedure developed by us: freshly calcined CaO dissolved in water and subjected to ultrasonic treatment for cleavage conglomerates. Thereafter, the two solutions were prepared comprising the half amount of the obtained calcium hydroxide, diammonium phosphate and ammonium phosphate concentrations with appropriate stoichiometric relationship.

Synthesis was carried out according to the reactions:



After decanting the mixture was heated in a microwave oven to adjust the temperature of 37 degrees, stirring was conducted by bubbling air, and then adjusted to pH 7, and was left to stand in the mother liquor for 48 hours at 37 °C. The precipitate was then thoroughly washed and dried at a temperature of 105 °C.

According to X-ray diffraction shown in Figure 1 in the crystalline phase sample application 1–6 corresponds to HA with a unit cell $\text{Ca}_5(\text{PO}_4)_3\text{OH}(\text{hex})$. Most crystallized sample is obtained under the designation HA-6. The reaction product is HA and β -TCP (< 20 %).

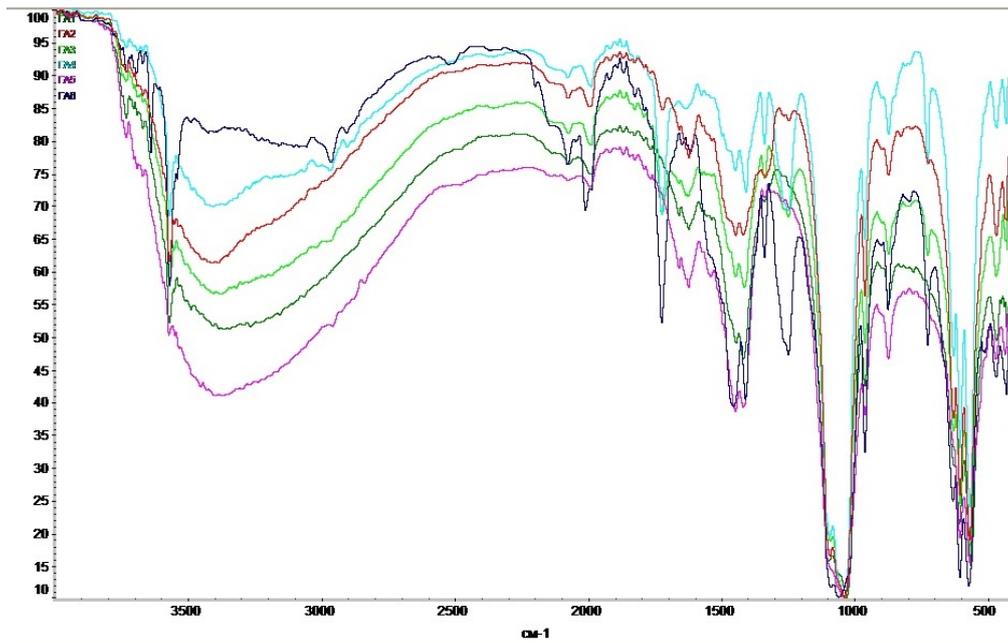


Fig. 2. FT-IR samples HA-1, HA-2, HA-3, HA-4, HA-5, HA-6

The IR spectra of all samples (Fig. 2) defined bands corresponding to vibrations of the phosphate groups in the range of wave numbers 955-962, 520-660 and 1020-1080 cm^{-1} .

The low intensity of the band at 3570 cm^{-1} and 630 cm^{-1} , corresponding to stretching and deformation vibrations of OH groups of HA in samples 1,2,3,5 indicates low levels of HA phase. Fluctuations corresponding bands in the ranges 870–875 cm^{-1} and 1300–1500 cm^{-1} belong to the C = O groups in the carbonate. The presence of carbonate groups in the structure of the samples associated with the adsorption of carbon dioxide from the air atmosphere during synthesis.

Thus, it is shown that the synthesis of 6 is most optimal to obtain a single-phase powder GA with minimal time and labor costs. Since the samples 1,2,3,4 and 5 showed no apparent efficacy, further examples will not be considered, however, sample number 1 is considered as a control.

Determination of the solubility is a very important step in the study of the properties of biomaterials based on calcium phosphate, as it allows to evaluate the ability of materials to resorption, i.e. dissolving in body fluids.

Table 1 shows the results of Dissolution samples HA-1 and HA-6 in saline solution at room temperature of 20 °C and the body temperature 37 °C.

Table 1. HA powders Solubility in physiological saline at pH 7, ω (NaCl) = 0,9 %

The concentration of ions Ca^{2+} in relatively saturated saline HA		HA-1	HA-6
$C_{\text{Ca}^{2+}} \cdot 10^3$, моль/л	20 °C	$1,19 \pm 0,03$	$1,59 \pm 0,03$
	37 °C	$1,33 \pm 0,02$	$1,74 \pm 0,04$

Conclusions:

1. Various methods of synthesis of hydroxyapatite were investigated, conducted a comparative analysis, based on the assumptions that had arisen in the course of the synthesis of its own synthesis was developed by known techniques: of the synthesis the own synthesis was developed using known techniques.
2. New method was developed for the rapid phase synthesis of hydroxyapatite using microwave radiation and mild conditions. The use of microwave radiation allows to obtain single phase HA powders affecting its properties: average particle size decreases from 200 nm to 80 nm, increasing the uniformity of the particles in the form and degree of polydispersity ranges from powders (50-120) nm to (20-40) nm; powders specific surface from $44 \text{ m}^2/\text{g}$ to $106 \text{ m}^2/\text{g}$; solubility in saline solution powders (CCa^{2+} , mol/l) from $(1,19 \pm 0,03) \cdot 10^{-3}$ to $(1,59 \pm 0,03) \cdot 10^{-3}$ at 20 °C and from $(1,33 \pm 0,02) \cdot 10^{-3}$ to $(1,74 \pm 0,04) \cdot 10^{-3}$ at 37 °C.

References

1. Barinov S.M., Kozlov V.S. «Bioceramics of calcium phosphate», 2012.
2. Safronova T.V., Shehirev M.A., Ceramic materials based on hydroxyapatite, obtained from solutions of different concentrations, Moscow State University, Inorganic Materials, 2007, t-43, № 8, p. 1005–1014.
3. Safronova T.V., Putlyayev V.I., Synthesis of nanocrystalline hydroxyapatite calcium from calcium saccharate and ammonium hydrogen phosphate, Report of the Academy of Sciences, 2009, t-426, № 4. – p. 491–496.
4. Bulanov E.N. Obtaining and study on nanostructured biocompatible materials based on hydroxyapatite. – Nizhny Novgorod: Nizhny Novgorod State University, 2012. – 103 p.